Mineral Analysis

Acid digestion

Mineral Sampling - definitions

- Rock – a naturally occurring collection of minerals combined to form a mass or aggregate that constitutes a significant part of the earth's crust.
- Mineral – the crystalline grains which make up a rock
- Ore – a collection of minerals that can be mined for profit
- Gangue – the worthless part of the ore sample. These can be minerals that are uneconomic to extract from the main ore body.
- Sulphide – a mineral containing one or more metallic elements with the chemical element sulphur. (e.g. Chalcopyrite, $CuFeS_2$)
- Oxide – a mineral containing one or more metallic elements with the chemical element oxygen. (e.g. Hematite, Fe_2O_3)
- Matte – a complex sulphide or mixture of sulphides
- Refractory – minerals that do not significantly change chemically at high temperatures and conditions

Mineral Sampling - minerals

- Minerals are made from a combination of the 92 naturally occurring chemical elements in the earth.
- These minerals can be hard and form natural crystals.
- There are thousands of minerals that occur within the earth's crust, but the four most common found in rocks include:
  - Quartz: colourless to white crystals, SiO_2

Mineral Sampling - minerals

- Feldspar: white (Na feldspar – plagioclase) or pink (K feldspar – orthoclase, $KAlSi_3O_8$) crystals made of SiO_4 units.

Mineral Sampling - minerals

- Mica: a soft flakey mineral often found in sheets in rocks. Granite contains 20 – 40% quartz, some feldspar and mica and some other minerals depending on the type of granite.

Mineral Sampling - minerals

- Mafic minerals: these include the dark coloured (mafic) minerals such as
  - Olivine – greenish glasslike mineral found in basalts. It has an approximate formula $(Mg,Fe)_2SiO_4$

Mineral Sampling - minerals

- Pyroxene – fibre like crystals with the general formula R_2SiO_4. (R= Ca or Mg)

Mineral Sampling - minerals

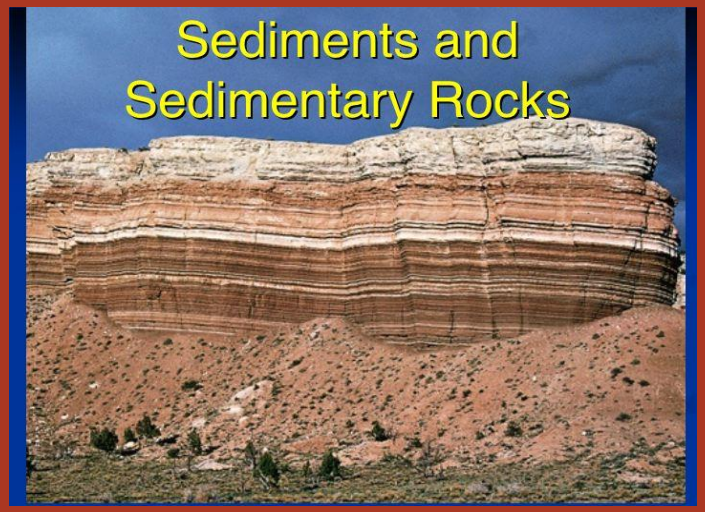
- Amphiboles – similar to pyroxenes except they contain (OH) or halogen (F, Cl) groups and are double chain silicates, as opposed to the single chained pyroxenes. (e.g. Asbestos minerals)

Basic Geology

- Igneous rocks
  - Rocks which have crystallised from a molten state after been intruded into other rocks (e.g. Granites), or extruded at the earth's surface (e.g. Volcanic rocks such as basalts).

Basic Geology

- Sedimentary rocks
  - when igneous rocks weather near the earth's crust fine grains are formed.
  - these accumulate by wind and water processes to form sediments.
  - these cement together to form rocks (e.g. sandstone, conglomerate, limestone).
  - the natural cement of limestone is calcite.



Basic Geology

- Metamorphic rocks
  - When igneous or sedimentary rocks are subjected to high temperatures and pressures within the earth, they alter to form new rocks.
  - E.g. Granite forms gneiss, sandstone forms quartzite, limestone forms marble.
  - Metamorphic rocks can be worn away to form new sedimentary rocks, as can igneous and old sedimentary rocks.

Stages of Analysis

- Definition of the problem
  - Analyst to decide what analytical information is needed
- Choice of method
  - What information is required and how it is to be obtained
- Sampling
  - Involves the process of selecting and removing a small, representative part of the whole, on which analysis will be performed
  - Sampling is the most critical part of the analytical process
- Sample pretreatment and separation
  - Sample converted into a suitable physical and/or chemical form prior to analysis

Stages of Analysis

- Calibration
  - Involves obtaining raw analytical data from suitably prepared standards
- Measurement
  - Occurs when the raw analytical data is obtained from measurements on the pre-treated sample
- Evaluation
  - Leads to meaningful analytical results from the raw data obtained from *calibration* and *measurement*
- Action
  - Occurs when the results are used to make decisions with respect to the original problem

Sample Preparation - acid digestion

- Hydrochloric acid (HCl)
  - Basic solvent in the analysis of ores and minerals
  - Its advantage is its easy volatility and solubility of most of its salts in water
  - Its disadvantage is when the solution is evaporated to low volume, the following species are volatile and hence lost from the digest: Ge^{IV}, As^{III}, Sb^{III}, Sn^{IV}, Se^{IV}, Hg^{II} , Au^{III}
  - Carbonates are easily dissolved using HCl.
    - A part of the carbonate material sometimes remains due to the presence of silica, pyrite, graphite and insoluble silicates.
  - HCl will partially dissolve some iron oxide minerals (e.g. Hematite, Fe_2O_3).
  - Some refractory forms of iron oxide (Magnetite, Fe_3O_4) will remain unattacked by HCl

Sample Preparation - acid digestion

- Nitric acid (HNO_3)
  - Powerful solvent for a number of minerals, whether dilute or concentrated.
  - Suited to sulphides and phosphates.
    - Oxidises sulphides to sulphates
    - Sulphur in sulphide ores must be oxidised at room temperature with dilute acid only, otherwise elemental sulphur results.
    - This prevents quantitative analysis of elements being sought.
  - Is rarely used on its own
  - Mainly used in combination with other acids/reagents.
    - Used in combination with HCl to form aqua regia
    - Solvent used to dissolve gold from its ore
  - Dissolves most metals found in nature, except gold and platinum.
  - It readily dissolves silver and palladium.

Sample Preparation - acid digestion

- Perchloric acid ($HClO_4$)
  - Similar properties to sulphuric acid
  - Has a high b.p. and is a powerful oxidizing and dehydrating agent at elevated temperatures (~200 deg. C)
  - It is useful in the decomposition and determination of silicon dioxide (SiO_2) in calcite ($CaCO_3$), dolomite and magnesite.
  - Conc. $HClO_4$ is a better solvent than conc. H_2SO_4 for the determination of monazite
  - Strict guidelines must be adhered to when handling $HClO_4$, due to the risk of fire or explosion, especially in the presence of organic material.

Sample Preparation - acid digestion

- Hydrofluoric acid (HF)
  - Only acid to dissolve silicate minerals in ore, converting the silicon containing mineral to volatile SiF_4
  - Has a strong affinity for beryllium, boron, scandium, aluminium and iron amongst some other transition metals.
  - Must be stored in teflon bottles due to its ability to corrode glass.
  - Useful in combination with other reagents
  - Warning: Requires stringent OHS procedures, engineering controls, relevant traing and SOPs to prevent exposure to the chemical.

Sample Preparation - acid digestion

- Bromine (Br_2)
  - Strong oxidising agent
  - Highly corrosive
  - Forms HBr in solution
  - Used to oxidise sulphur to sulphate
  - Oxidise volatile arsenic, antimony, selenium species to non-volatile forms of these elements.
  - Warning: safety issues!

Sample Preparation - acid digestion

- Sulphuric acid (H_2SO_4)
  - Hot concentrated sulphuric acid has a weak oxidising effect in the dissolution process.
  - It oxidises not only metals, but also sulphur and coal, which are oxidised with the evolution of sulphur dioxide gas.
  - Useful for the dissolution of sulphides, fluorosilicates, and minerals containing niobium, tantalum, titanium and zirconium.
  - Hot concentrated H_2SO_4 is used in the decomposition of sulphide arsenic, antimony and tin minerals, metallic arsenic and antimony

Sample Preparation - acid digestion

- Acid mixtures:
  - Aqua regia (nitrohydrochloric acid)
    - Useful for the dissolution of ores containing gold, silver and platinum.
    - 1 part HNO_3 : 3 parts HCl
    - Powerful oxidizing agent
    - Suitable for some ‘speciation’ analysis
  - Nitrosulphuric acid ($HNO_3 + H_2SO_4$)
    - Determination of uranium in rare earth oxides
  - Perchlorosulphuric acid ($HClO_4 + H_2SO_4$)
    - Used to dissolve highly resistant minerals (e.g. Chromospinelides with Fe, Cr, Zn, Mn, Ti, V as main components).

Sample Preparation - acid digestion

- Nitroperchloric acid (HNO_3 + $HClO_4$)
  - Used in wet ashing digestion techniques
  - Strong oxidizing agent
  - HNO_3 oxidises the readily oxidisable material, while the $HClO_4$ oxidises the resistant material
- A mixture of hydrochloric, sulphuric and perchloric acids is an efficient solvent for nickel and iron ores
- A multi-acid digest using nitric, bromine, perchloric and hydrofluoric acid is an excellent solvent for most minerals. Hydrochloric acid is used to dissolve the residue at the completion of the digest.

Sample Preparation - fusion

- Fusion - to ‘bring together’ at high temperatures
- Effective in the structural breakdown of resistant minerals
- Use of a flux is required to bring about sample decomposition
- Fusion results in the formation of some soluble and insoluble products
- By acidifying the resultant solution, most elements may be analysed by instrumental or in some cases, by classical means
- The main advantage of decomposition by fusion, compared to decomposition with acids, is due to the effect of high temperature, which cannot be achieved in an aqueous solution.

Sample Preparation - fusion

- Fusion techniques usually involve accurate weighing of the sample into a crucible
- The sample is roasted at 600 deg. C to remove volatile elements such as:
  - Sulfur (as sulphur dioxide)
  - Arsenic (as arsenic trioxide – smell of garlic)
  - Antimony (as antimony trioxide)
  - Phosphorus
  - Carbon (as oxides of carbon)
  - Mercury
- Once these elements are removed, the sample is converted into an oxide, which aids in the fusion process.

Sample Preparation - fusion

- Sodium peroxide
- Sodium Carbonate
- Lithium metaborate/tetraborate
- Potassium hydrogen sulphate

Sample Preparation

- Samples require decomposition in order to obtain them in solution form:
  - Metals are decomposed in suitable acids:
    - HCl – Zn, Cd (slow), Al (dependant on particle size), Ti (slow; requires heating), Sn, Fe, Co, Ni, Mn
    - HNO_3 (oxidizing acid) – Cu, Ag, Hg, Zn, Cd, Pb, Bi, Cr (slow), Mo, Fe, Ni, Co, Mn
    - H_2SO_4 – alternative to HNO_3. Dissolves Al slowly.
    - HCl/HNO_3 (3:1 ratio) – Aqua Regia. Semi quantitative digest. Useful for Au, Pt.

Sample Preparation

- Mineral digestion:
  - dependent on mineral type.
  - this is not always known.
  - digestion of minerals involves use of a combination of acids or a stepwise digestion approach.
  - total digest involves $HNO_3/Br_2/HF/HClO_4$ with a final addition of HCl at the completion of the procedure.
  - This method is suitable for most minerals except refractories such as the spinels (magnetite Fe_3O_4, ilmenite $FeO.TiO_2$ and chromite $FeO.Cr_2O_3$) and rare earths.

Sample Preparation

- Mineral digestion:
  - Resistant minerals to acid attack are filtered, collected in a crucible and fired in a furnace at a set temperature (680°C-700°C) with a suitable flux to bring about a fusion reaction. The fusion product is then dissolved in acids and added to the remainder of the decomposed ore.
  - Minerals containing silica require HF/ H_2SO_4 mixtures to dissolve.
  - Use of Teflon or platinum ware must be used (NOT glass).
  - Stringent safety precautions must be adhered to when HF is in use.

Sample Preparation

- Samples containing organic matter:
  - Wet ashing
    - Involves dissolving in a $HNO_3/HClO_4$ mixture. HNO_3 oxidises the readily oxidisable material, while the $HClO_4$ oxidises the resistant material.
    - CAUTION:
      - Use special fume hoods to remove the $HNO_3/HClO_4$ fumes
      - No organic solvents to be present!
      - No wood material to be stored in fumehood during the digestion! Explosions and/or fire may result.
      - Do not spray solutions containing $HClO_4$ into the flame of an AAS. Solutions containing high copper concentrations and $HClO_4$ are known to explode in an AAS.

Sample Preparation

- Samples containing organic matter:
  - Dry ashing
    - Oxidise the organic material by placing sample in a furnace that has a suitable air or oxygen flow present.
    - The organic matter oxidises to CO_2, H_2O and other volatiles.
    - Disadvantage: Volatile elements are lost in the analysis if required (e.g. P, S, Se, Te, Hg, As).

Separation

- This step is usually done to obtain a pure substance or to separate the analyte from interfering substances.
- Methods of separation include:
  - Precipitation
  - Volatilisation
  - Chromatography
  - Extraction
- Precipitation and chromatography are commonly used in organic analysis.
- Volatilisation and extraction are used in inorganic analysis as a method of preconcentration.
- Precipitation also finds application in inorganic analysis when concentrations of an analyte are very high.

Preconcentration

- Preconcentration is required when the concentration of an analyte is below the detection limit of the analytical instrument.
  - Evaporation of the solvent is a simple method of preconcentration.
    - May lead to loss of sample.
    - Is difficult to control
    - Can be dangerous (e.g. $HClO_4$ mixtures)
  - The preferred technique is liquid-liquid extraction or solvent extraction.

Solvent Extraction

- Solvent extraction involves:
  - Chelation followed by
  - Extraction into an organic layer

- Chelation is the combination of a cation with one or more ligands to form a complex.
- If the complex is uncharged it tends to be more soluble in organic solvents, rather than aqueous layers.
- Example -
  - Au-DIBK system:
  - Au (aq.) = 0.05ppm → Au (org.) = 5ppm

Activity Series

K	React with cold water and acids (HCl….)
Ca	
Na	
Mg	React with steam and acids (HCl; HNO_3)
Al	
Mn	
Zn	
Fe	
Cr	
Cd	
Co	Can react with acids (HNO_3; H_2SO_4)
Ni	
V	
Sn	
Pb	
H	
Cu	HNO_3
Hg	
Ag	
Au	HCl/HNO_3
Pt	

Week 1 task

- Using the internet +/or the MSDS, find information for the reagents being used in the course:
  - Hydrochloric acid (conc.)
  - Nitric acid (conc.)
  - Di-iso butyl ketone (DIBK)
  - Sodium peroxide
- Information required includes:
  - Alternate name/s
  - Chemical formula
  - UN number
  - Hazards (include incompatibility with other substances)
  - Recommended PPE
  - Environmental concerns